Assessing the Scope of the Introduction of Schiff Bases as Co-Ligands for Monometallic and Homobimetallic Ruthenium Ring-Opening Metathesis Polymerisation and Ring-Closing Metathesis Initiators

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Abstract: A new class of homobimetallic and monometallic Schiff base-substituted ruthenium olefin metathesis catalysts has been prepared, characterised and tested in ring-closing metathesis (RCM) and ring-opening metathesis polymerisation (ROMP) reactions. The results obtained point out that the synergy of Schiff base ligands with coordinatively labile ligands leads to bimetallic catalytic systems that combine very high activity with excellent stability. Furthermore, the catalytic activity of these catalysts is very dependent on the steric and electronic environment of the Schiff base. To conclude, a mechanism that explains the obtained data is postulated.

Keywords: bimetallic catalysts; homogeneous catalysis; ring-closing metathesis; ring-opening metathesis polymerisation; ruthenium and compounds

Introduction

In the 34 years since the landmark report by Calderon and coworkers that both ring-opening polymerisation and the disproportionation of acyclic olefins were the same reaction,[1] olefin metathesis has become one of the most intensively investigated fields of research[2] and this because of the central importance of carbon-carbon bond formation in both organic synthesis and polymer chemistry. Especially during the last decade the reaction has experienced a tremendous breakthrough due to the development of efficient molybdenum[3] and ruthenium[4] catalysts having sufficiently well-balanced electronic and coordinative unsaturation to allow convenient use and high turnover performance. These new generations of olefin polymerisation catalysts have catapulted the polymer industry into a new area. Ring-opening metathesis polymerisation (ROMP) has opened new synthetic routes to a variety of polymeric materials producing polymers with attractive mechanical and electrical properties.[5] There has also been a rapid embrace of these catalysts as tools for organic fine chemicals synthesis. Indeed, especially the broad scope and reliability of the ring-closing metathesis (RCM) reaction has greatly simplified the total synthesis of a wide variety of architecturally complex natural and unnatural products.[6] In comparison with the ruthenium-based catalytic systems, the molybdenum systems developed by Schrock and coworkers (complex **A**, Figure 1) are significantly more reactive towards a broad range of substrates with many steric or electronic variations. Critical drawbacks of these Mo-based carbene complexes are, however, their moderate to poor functional group tolerance, high sensitivity to air, moisture or even to trace impurities in solvents, thermal instability on storage and expense of preparation.[2h,3,5a,7] In contrast to the early transition metal molybdenum catalysts, the ruthenium complexes developed by Grubbs and coworkers (complex **B**, Figure 1) possess remarkable tolerance towards most functional groups and a diminished sensitivity to atmospheric oxygen and water. Moreover, they can be conveniently stored even under an air atmosphere without severe decomposition for several weeks.[2h,5a,8] Recently, three groups almost simultaneously reported on the preparation and catalytic properties of N-heterocyclic carbene ligand-containing complexes (complex **C**, Figure 1) exhibiting metathesis activity comparable to that of the molybdenum complex **A**, yet having a remarkable air and water stability similar to that of the parent benzylidene complex **B**.[9] In 1999 Herrmann and coworkers reported on the synthesis and catalytic activity of the metathesis initiator **D** (Figure 1).[9g,9i]

This complex that combines an imidazolin-2-ylidene ligand with a bimetallic catalyst system, is one of the fastest metathesis initiators known so far. However, the
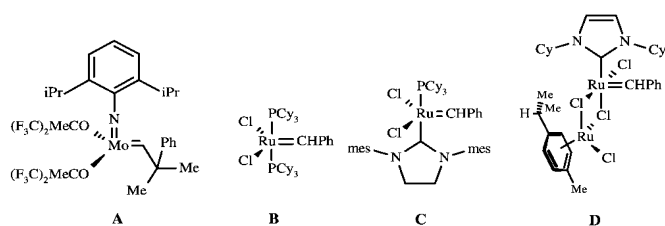
Figure 1.

corresponding propagating species of this system is too short-lived to take metathesis reactions of difficult substrates to completion.[10]

In 1998 Grubbs et al. reported on the exceptional stability of Schiff base-substituted analogues of complex **B**.[11] As part of our systematic investigation on the ruthenium(II)-Schiff base chemistry in various organic reactions[12] and driven by the search for finding a well-defined olefin metathesis initiator possessing the ideal balance between activity and stability, we came to the idea of incorporating a Schiff base-substituted ruthenium centre in a bimetallic structure. Herein we report that it is the combination of coordinatively more labile ligands with Schiff base ligands on the ruthenium centre that allows the class of bimetallic ruthenium catalysts to develop their full commercial potential.

Results and Discussion

The 12 different catalytic systems for which the catalytic performance in ROMP and RCM reactions was assessed, are depicted in Scheme 1. In the experimental section the details of the synthesis are given.
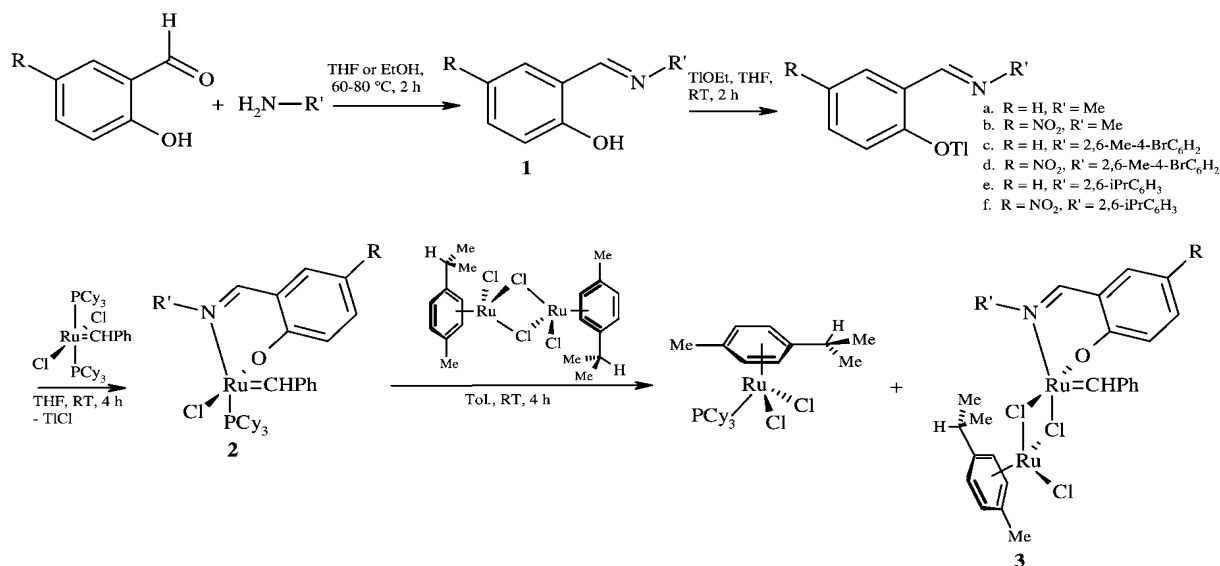
In a first set of experiments, the catalytic activity of the Schiff base substituted ruthenium benzylidenes **2a–f** and **3a–f** is checked for ROMP with some representative monomers. The yields [%] of the formed polymers are depicted in Table 1.
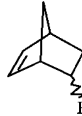
It is obvious from Table 1 that both catalytic systems **2** and **3** succeed in performing ROMP reactions with the monomers tested, although significant differences in their behaviour were noticed. For the catalytic systems **2** the observed conversion sequence is **2b** > **2a** > **2d** > **2c** > **2f** > **2e** whereas for the bimetallic initiators conversion sequence is reversed, **3e** > **3f** > **3c** > **3d** > **3a** > **3b**.

These results show that for both the monometallic systems **2** as for the bimetallic systems **3** the bulkiness of the Schiff base and the electron-withdrawing properties of the Schiff base substituents exert a profound influence on the ROMP activity. For instance, phenylnorbornene is converted in 98%, 80%, and 69% yield for **2a**, **2c**, and **2e**, respectively, and in 19%, 61%, and 100% yield, respectively, for **3a**, **3c**, and **3e**. These results also show that the introduction of more bulkiness in the Schiff base is beneficial for the systems **3** but detrimental for systems **2**. The influence of the electronic environment of the Schiff base is best illustrated by comparing the catalytic performance of system **2a** with that of **2b**, **2c** with **2d**, **2e** with **2f**, **3a** with **3b**, **3c** with **3d**, and **3e** with **3f**. In the monometallic series, the complex bearing the electron-withdrawing nitro substituent (**2b**, **2d**, and **2f**) reaches substantially higher conversions whereas for the bimetallic complexes the opposite is observed. Furthermore, it is clear that for both types of initiators the bulkiness of the Schiff base has a greater impact on catalytic performance in ROMP reactions than the electronic influence exerted by the Schiff base substitu-

Scheme 1. Synthesis route of the different catalytic systems.

Table 1. Yield (%) for ring-opening metathesis polymerisation of some representative monomers using catalytic systems **2a – f** and **3a – f** (for details concerning the reaction conditions, see experimental section).

Substrate	Catalytic system					
	2a/3a	**2b/3b**	**2c/3c**	**2d/3d**	**2e/3e**	**2f/3f**
Cyclooctene	96/*31*	100/*23*	90/*76*	92/*64*	86/*100*	89/*90*
	Norbornene derivatives (*endo* and *exo*)					

	2a/3a	**2b/3b**	**2c/3c**	**2d/3d**	**2e/3e**	**2f/3f**
R = H	100/*59*	100/*48*	100/*87*	100/*78*	100/*100*	100/*96*
R = ethyl	100/*41*	100/*33*	100/*79*	100/*66*	100/*100*	100/*91*
R = butyl	100/*34*	100/*24*	95/*70*	98/*61*	91/*100*	93/*84*
R = hexyl	100/*18*	100/*11*	92/55	97/*49*	89/*100*	92/*73*
R = decyl	100/*9*	100/< 5	88/*34*	93/*20*	81/*100*	87/*56*
R = ethylidene	100/*37*	100/*26*	84/*72*	91/*63*	76/*100*	81/*94*
R = phenyl	98/*19*	100/*15*	80/*61*	88/*50*	69/*100*	77/*86*
R = cyclohexenyl	95/*13*	100/*12*	77/55	85/*46*	66/*100*	73/*81*
R = ethylnorbornane	100/*41*	100/*36*	95/*76*	96/*67*	79/*100*	88/*83*
R = cyano	31/9	38/< 5	11/27	17/*19*	< 5/66	8/*43*
R = hydroxymethyl	38/*15*	43/< 5	19/*39*	23/28	12/*74*	17/*51*
R = chloromethyl	100/*51*	100/*36*	98/*85*	100/*67*	81/*100*	87/*97*
R = triethoxysilyl	100/*43*	100/*29*	92/*71*	97/58	77/*100*	82/*89*

Table 2. Properties of the polymers formed with the most performance initiators, **2b** and **I3e**, of both types of catalysts **2** and **I3**.

Substrate	2b/*3e*			
	M_n ($\times 10^3$)[a]	PDI[a]	σ_c[b]	f_i[c]
Cyclooctene	24/*29*	1.86/*1.49*	0.48/*0.46*	0.92/*0.76*
	Norbornene derivatives			

	M_n ($\times 10^3$)[a]	PDI[a]	σ_c[b]	f_i[c]
R = H	84/*95*	1.51/*1.37*	0.25/*0.22*	0.90/*0.79*
R = ethyl	111/*138*	1.63/*1.35*	0.22/*0.21*	0.88/*0.71*
R = butyl	138/*183*	1.55/*1.31*	0.24/*0.29*	0.87/*0.66*
R = hexyl	176/*207*	1.62/*1.37*	0.22/*0.18*	0.81/*0.69*
R = decyl	223/*257*	1.58/*1.29*	0.26/*0.25*	0.84/*0.73*
R = ethylidene	112/*137*	1.70/*1.39*	0.19/*0.21*	0.86/*0.70*
R = phenyl	170/*206*	1.68/*1.36*	0.29/*0.27*	0.80/*0.66*
R = cyclohexenyl	168/*188*	1.62/*1.41*	0.27/*0.27*	0.83/*0.74*
R = ethylnorbornane	186/*225*	1.66/*1.39*	0.18/*0.23*	0.81/*0.67*
R = cyano	66/*123*	1.52/*1.27*	0.22/*0.18*	0.55/*0.51*
R = hydroxymethyl	74/*153*	1.57/*1.33*	0.26/*0.24*	0.58/*0.48*
R = chloromethyl	136/*158*	1.71/*1.40*	0.24/*0.29*	0.84/*0.72*
R = triethoxysilyl	236/*277*	1.58/*1.36*	0.27/*0.31*	0.87/*0.74*

[a] M_n and the polydispersities (PDI) are determined by size-exclusion chromatography (SEC) with polystyrene calibration.
[b] Fraction of polymers with *cis* configuration.
[c] f_i = initiation efficiency = $M_{n, theor.}/M_{n, exp.}$ with $M_{n, theor.}$ = ([monomer]$_0$/[initiator]$_0$) × MW(monomer) × conversion.

ents. The properties of the polymers obtained with the highest performing initiators for both classes of catalytic systems, namely **2b** and **3e**, are depicted in Table 2.

From Table 2 one observes that for system **2b** the polydispersity index (PDI) of the formed polymers is much higher in comparison with the PDI of the polymers obtained with the bimetallic complex **3e**. This indicates that in the latter case the polymerisations have a more living character. It is also remarkable that the number average molecular weights (M_n) are much higher in the case of the bimetallic system, meaning that the initiation efficiency is lower (Table 2). A *trans* configuration of the

Table 3. Yield (%) for RCM of some representative substrates using catalytic systems **2a – f** and **3a – f**.[a]

Entry	Substrate[b]	Product	2a/3a	2b/3b	2c/3c	2d/3d	2e/3e	2f/3f
1			100/*100*	100/*100*	100/*100*	100/*100*	100/*100*	100/*100*
2			< 5/*13*	< 5/ < 5	< 5/*58*	9/*44*	18/*83*	21/*72*
3			< 5/*6*	< 5/ < 5	< 5/*41*	6/*29*	11/*62*	17/*49*
4			100/*100*	100/*100*	100/*100*	100/*100*	100/*100*	100/*100*
5			100/*100*	100/*100*	100/*100*	100/*100*	100/*100*	100/*100*
6			40/*40*	44/*31*	47/*71*	59/*67*	68/*96*	76/*89*
7			12/*32*	13/*25*	18/*69*	25/*66*	41/*87*	56/*74*

[a] For details concerning the reaction conditions see experimental section.
[b] E = COOEt.

polynorbornene derivatives and polycyclooctene is predominant, irrespective the catalytic system used. This is in accordance with the general observation for ruthenium catalysts in ROMP reactions.

In a second set of experiments, the performance of the two classes of catalytic systems was tested in RCM reactions. Table 3 summarises the RCM results obtained with some representative substrates.

First of all it needs to be mentioned that the difference in reaction temperature between the monometallic and the bimetalllic systems is a result of the observation that for the bimetallic catalytic systems already very good conversions were obtained at a temperature of 55 °C, whereas preliminary tests pointed out that the mono-metallic catalytic systems could only exploit their full potential at a temperature of 70 °C.

When analysing the results gathered in Table 3, one observes the same order in catalyst performance for RCM and ROMP reactions for the bimetallic catalytic complexes. For instance, the tetrasubstituted malonate derivative (Entry 3, Table 3) is converted with 6%, < 5%, 41%, 29%, 62%, and 49% with systems **3a, 3b, 3c, 3d, 3e**, and **3f**, respectively. The conclusions about the steric bulk of the Schiff base ligands and the electron-withdrawing properties of the Schiff base substituents that were made for the ROMP reactions with this type of catalyst can also be drawn here. For the monometallic catalysts, however, a totally different behaviour in ROMP and RCM reactions is observed. As opposed to ROMP, RCM activities generally decrease in the

order of **2f** > **2e** > **2d** > **2c** > **2b** > **2a**. When comparing the electronic influence for the same series of catalysts, the same trend is observed as for ROMP. Indeed, **2f** has a higher activity than **2e**, **2d** has a higher activity than **2c**, and **2b** has a higher activity than **2a**. However, examining steric effects, a totally different behaviour is observed. In this case, introduction of more steric bulk in the Schiff base ligand leads to an increase in RCM activity. Indeed, catalytic performance increases in the order of the series **2e, f** > the series **2c, d** > the series **2a, b**.

To explain the influence of steric bulk and electronic contribution of the Schiff base ligands and the difference or analogy in reactivity between ROMP and RCM reactions for both types of catalysts **2** and **3**, the mechanism for metathesis reactions is depicted in Scheme 2. In accordance with the proposed mechanism for ruthenium benzylidene complexes **B, C**, and **D** from Figure 1[13], the mechanism of the ligand substitution for both types of initiators **2** and **3** with olefinic substrate is proposed to take place in a dissociative fashion.

The fundamental difference however, lies in the fact that for the monometallic complexes of class **2** it is suggested that the mechanism involves the decoordina-tion and coordination of "one-arm" of the bidentate Schiff base ligand instead of the usual PCy_3 dissociation as for the systems **B** and **C**. This dissociation of the N-bonded arm of the chelating salicylaldimine ligand is proposed for the following reasons: (1) addition of CuCl, a well-known phosphine scavenger, to solutions of
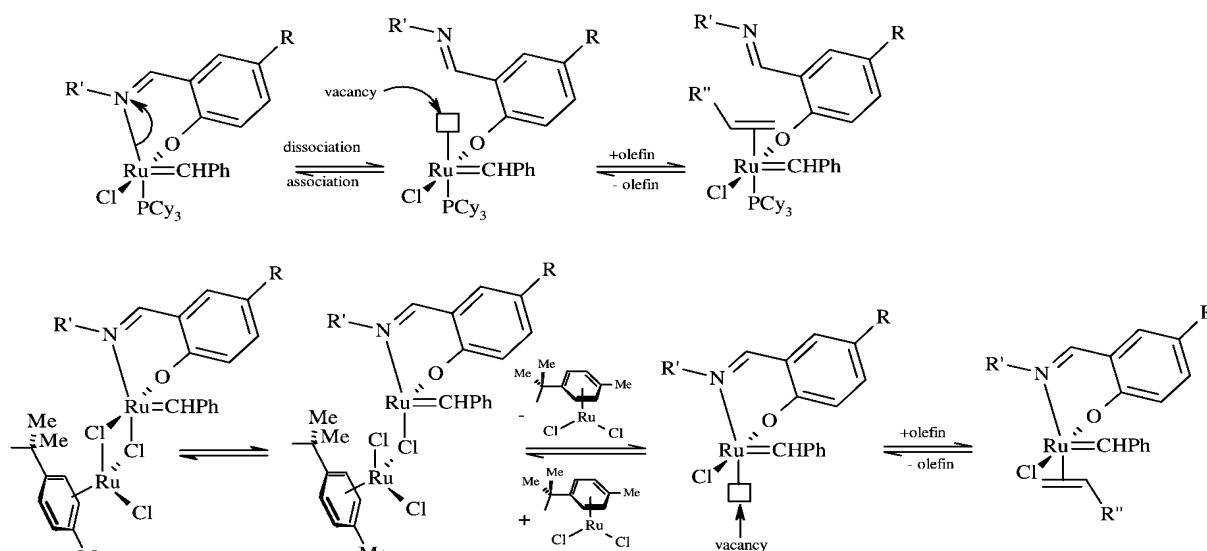
Scheme 2. Mechanism for metathesis reactions with catalytic systems **2a–f** and **3a–f**.

several catalysts of type **2**, in the presence of an olefin substrate did not result in a noteworthy increase of activity both in ROMP and RCM reactions. (2) When nitrogen donors are used as co-ligands in combination with phosphorus as donors, the so-called *trans* effect[14] must be taken into account. In a given complex one can have a substitutionally inert, coordinated phosphane ligand and *trans* to this P-donor, a kinetically labile ligand. For complexes combining a nitrogen and a phosphorus donor in their coordination sphere, this *trans* effect will play a decisive role in the dissociation behaviour of both ligands because the difference in electron-donating properties of both ligands is small.[15,16] One should not take into account a dissoci-ation of the O-bonded arm of the salicylaldimine ligand because this O is not in a *trans* position to the phosphorus and because in general, [Mt]-O bonds are much stronger than [Mt]-N bonds.[17] (3) The "hard and soft acid-base theory" can also be used to explain a favourable dissociation of the nitrogen donor over the phosphorus donor. The fairly soft late-transition metal ruthenium will prefer to bond with the softer P-donor instead of with the harder N-donor.[18] (4) In general, the most stable organometallic compounds are those in which all low-energy orbitals are involved in (prefera-bly) two-electron bonding. This implies an absence of unpaired electrons on the metal centre which is fulfilled when the metal centre has an even number of electrons and when the complex is of the low-spin type, that is, one where there is maximum pairing of all the available metal d electrons.[19] It is a well-known fact that, in general, nitrogen donors are not as effective in produc-ing low-spin complexes with the consequence that the species produced are less thermodynamically stable and more kinetically labile than their low-spin analogues

with P-donors.[20] (5) In general, [Mt]-N bonds are mainly of the σ-type and [Mt]-P bonds of σ- and π-types.[15,17] However, with ligands containing sp^2-hybri-dized nitrogen atoms, as is the case with Schiff base ligands, π-interactions and thus π-back-bonding effects can take place. Nevertheless, while their occurrence is beyond dispute, the extent to which these π-effects determine the binding properties between an sp^2-hybridized N-ligand and the metal remain much smaller than the influence that these π-effects exert on the binding properties between P-containing ligands and metal centres.[16] (6) The distinct influence of the steric bulk of the Schiff base ligands on catalytic performance of type **2** initiators is in line with the fact that the strength of [Mt]-N bonds is very much affected by steric effects.[21] (7) Further evidence for the mechanism of dissociation for type **2** catalytic systems was provided by transferring 0.5 mmol of the catalyst solution in C_6D_5Cl into a 15-mL vessel followed by the addition of 1 equivalent of norbornene solution in C_6D_5Cl. The reaction mixture was then heated at 70 °C. At regular time periods, NMR samples were taken from the reaction mixture and analysed *via* ^{31}P NMR. Despite careful monitoring of the reaction mixture, no evidence was found for the dissociation of the PCy_3 ligand.

The proposed dissociative mechanism for the bimet-allic type **3** initiators is in total agreement with the findings of Herrmann et al. with analogous bimetallic ruthenium complexes (e.g., complex **D** from Fig-ure 1).[13 (b)] Indeed, also Herrmann postulates a two-step dissociation mechanism with a sequential hetero-lytic cleavage of the two chloro bridges and liberation of the coordinatively labile ligand {(*p*-cymene)RuCl$_2$} as the key step in the olefin metathesis reaction pathway with first- and second-generation Grubbs-type bimetal-

lic ruthenium complexes. The *trans* effect of the chloro bond on the stability of the [Mt]-N bond should not be taken into account here because it is well-known that chlorine atoms exhibit a very weak *trans* labilising effect.[15] Thus, because of the absence of a ligand with strong labilising effect *trans* to the [Mt]-N bond, the lability of the {(*p*-cymene)RuCl$_2$} fragment and the possibility that the dissociation of the {(*p*-cymene)RuCl$_2$} fragment is assisted by the exothermic dimerisation reaction to give [(*p*-cymene)RuCl$_2$]$_2$,[13b] it is very reasonable to state that the bimetallic type **3** catalysts are able to populate the dissociative pathway just as readily as **D**.

By accepting the mechanisms depicted in Scheme 2, the observed activities of both type **2** and type **3** catalytic systems in ROMP and RCM can be explained. For the bimetallic type **3** complexes, the increasing activity in ROMP and RCM metathesis reactions with increasing bulk of the Schiff base ligand and the disadvantageous effect of the electron-withdrawing nitro substituent on the Schiff base makes perfect sense because, according to the proposed mechanism, the active intermediate (having a vacancy for olefin coordination) is stabilised or, respectively, destabilised when the steric and electronic parameters are altered in the above-mentioned way. For type **2** complexes, the profitable influence of the electron-withdrawing nitro substituent on the Schiff base for the activity of these complexes in RCM and ROMP reactions are in perfect agreement with the proposed mechanism. Indeed, by diminishing the electron density on the nitrogen atom, the "one-arm" decoordination of the chelating salicylaldimine ligand is stimulated. The opposite influence of the steric bulk on RCM and ROMP performance with this type of initiators can be understood when one bears in mind that in ROMP reactions the growing polymer remains attached to the metal centre. It is clear, for a certain degree of polymerisation, that the incoming new monomer will be severely hindered by this "polymer-tail" when the Schiff base is too bulky (Figure 2).

In RCM reactions the incoming new olefin substrate is never a problem because of the absence of such a "polymer-tail". On the contrary, the results gathered in Table 3 indicate that introduction of more bulkiness in the Schiff base ligand has a stabilising effect on the reactive intermediate (having the vacancy) and thus stimulates the "one-arm" decoordination of the bidentate salicylaldimine ligand.

The results gathered in Tables 1 and 2 also reveal that our mechanistic proposals are not affected by heteroatoms in the ROMP-monomers. The difference in conversion for cyano- and hydroxymethylnorbornene with catalysts **2b** and **3e** (respectively, 38% and 43% for **2b** and 66% and 74% for **3e**) can be explained by the initiator efficiencies for **2b** and **3e** with these monomers. Whereas for all monomers the initiator efficiencies vary between 0.7 and 0.8, they drop to 0.5–0.6 for the two
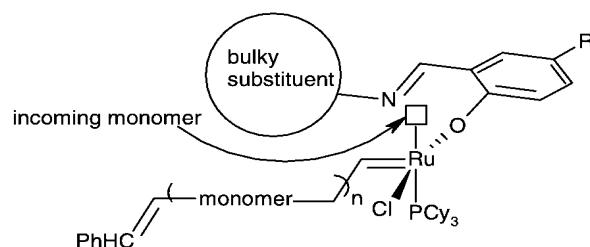
Figure 2. Illustration of the detrimental influence of steric Schiff bases on ROMP activity with catalytic systems **2**.

above-mentioned monomers. Moreover, the decrease is for both catalytic systems more or less the same leading to the conclusion that the detrimental effect of cyano or hydroxymethyl substituents is comparable for both systems. The difference in yield must be sought in the activity of the catalysts. It seems that the turnover frequency for **3e** (132 h^{-1} and 148 h^{-1} for, respectively, cyano- and hydroxymethylnorbornene) is substantially higher in comparison with **2b** (76 h^{-1} and 86 h^{-1} for, respectively. cyano- and hydroxymethylnorbornene) as **3e** reaches considerably higher conversions than **2b** with cyano- and hydroxymethylnorbornene within the same time period. These observations are in line with the observations that catalysts of type **C** (Figure 1) have remarkable lower turnover frequencies than the analogous bimetallic complexes of type **D** (Figure 1).[10]

The outstanding stability of the initiators of type **2** have already been demonstrated by Grubbs et al.[11] In order to assess the stability of the bimetallic type **3** catalytic systems, these systems were stored for one week in the solid state under an air atmosphere after which we tested them in ROMP reactions with phenylnorbornene. The results of these experiments indicated no noteworthy loss of performance. The same conclusion could be drawn when these complexes were transferred into a solution of chlorobenzene under inert atmosphere. Again, after one week, no loss of activity was revealed in ROMP experiments using phenylnorbornene as substrate.

Although we have purified the bimetallic catalytic systems (see experimental section), it should be mentioned that the stoichiometrically generated piano-stool-type complexes {Ru(*p*-cymene)PCy$_3$Cl$_2$} (see Scheme 1) do not affect catalyst activity and, in fact, do not need to be separated for routine usage.[22] Moreover, Demonceau et al. showed that these piano-stool-type complexes are extremely active in Atom Transfer Radical Polymerization (ATRP) reactions.[23] In addition, our laboratory succeeded in heterogenising these compounds on mesoporous and amorphous silica carriers leading to very active systems for ATRP.[24] So by following this heterogenising methodology developed in our laboratory, it is now possible to come to a highly active heterogeneous ATRP catalyst and a highly performing metathesis catalyst via one synthesis.

Conclusion

In conclusion, we have succeeded in synthesising and characterising a new class of homobimetallic ruthenium olefin metathesis catalysts exhibiting the best combination of stability and activity known so far for this type of catalyst. Moreover, we also synthesised, characterised, and tested the monometallic counterparts. In addition, we postulate a reasonable mechanism that explains all the observed results for both types of catalytic systems in ring-closing metathesis and ring-opening metathesis polymerisation reactions.

Further studies concerning the combination of ROMP and ATRP methodologies to make new polymers with interesting properties and further proof concerning the postulated mechanism depicted in Scheme 2, are currently under way.

Experimental Section

General

All reactions and manipulations were performed under an argon atmosphere by using conventional Schlenck-tube techniques. Argon gas was dried by passage through P_2O_5 (Aldrich 97%). ^{1}H NMR (500 MHz) spectra were recorded on a Bruker AM spectrometer. ^{13}C NMR (75.41 MHz) and ^{31}P NMR (121.40 MHz) spectra were recorded on a Varian Unity 300 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) with TMS employed as the internal solvent for proton spectra and 85% phosphoric acid employed as the external solvent. IR spectra were taken with a Mattson 5000 FTIR spectrometer. The number and weight average molecular weights (M_n and M_w) and polydispersity (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) (CHCl$_3$, 25 °C) using polystyrene standards. The GPC instrument used is a Waters Maxima 820 system equipped with a PL gel column. Elemental analyses were performed with Carlo Erba EA 1110 equipment.

The ruthenium dimer [RuCl$_2$(p-cymene)]$_2$ was prepared according to literature procedures[25] and the structure and purity were checked with IR and ^{1}H NMR and ^{13}C NMR spectroscopy. Cyclooctene and norbornene were purchased from Aldrich and distilled from CaH$_2$ under nitrogen prior to use. The other norbornene derivatives were purchased from INEOS and used as received. Commercial grade solvents were dried and deoxygenated for at least 24 h over appropriate drying agents under nitrogen atmosphere and distilled prior to use. Unless otherwise noted, all other compounds were purchased from Aldrich Chemical Co., and used as received.

General Procedure for Preparation of the Schiff Base Ligands 1a–f

The Schiff base ligands **1a–f** were prepared and purified using well-established procedures.[11]

The condensations of salicylaldehydes with aliphatic amine derivatives were carried out with stirring in THF at reflux

temperature for 2 hours. After cooling to room temperature, the viscous yellow oily condensation products were purified by silica gel chromatography (silica gel 60, 0.063–0.200 mm, Merck, a 5:1 benzene-tetrahydrofuran mixture was used as an eluant) and the desired salicylaldimine ligands were obtained in excellent yields. The condensations of salicylaldehydes with aromatic amine derivatives were carried out with stirring in ethanol at 80 °C for 2 hours. Upon cooling to 0 °C, a yellow solid precipitated from the reaction mixture. The solids were filtered, washed with cold ethanol and then dried under vacuum to afford the desired salicylaldimine ligand in quantitative yields.

Schiff base 1a: Salicylaldehyde (0.24 g, 2 mmol), methylamine (2.0 M solution in THF; 1 mL, 2 mmol) and THF (15 mL) afforded the compound as a yellow liquid. ^{1}H NMR (CDCl$_3$): δ = 12.96 (s, 1H), 8.75 (s, 1H), 7.50 (d, 1H), 7.15 (d, 1H), 7.27 (t, 1H), 6.78 (t, 1H), 3.30 (d, 3H); ^{13}C NMR (CDCl$_3$): δ = 166.4, 161.7, 137.0, 133.8, 120.8, 119.9, 118.4, 45.9; IR: ν = 3325 (ν$_{OH}$, br), 3061 (ν$_{CH}$, w), 2976 (ν$_{HC=N}$, w), 2845–2910 (ν$_{CH_3}$, br), 1623 (ν$_{C=N}$, s), 1573 [ν$_{C=C(Ph)}$, w], 1525 [ν$_{C=C(Ph)}$, w], 1497 [ν$_{C=C(Ph)}$, w], 1465 [ν$_{C=C(Ph)}$, w], 1125 cm^{-1} (ν$_{CO}$, br).

Schiff base 1b: 5-Nitrosalicylaldehyde (0.33 g, 2 mmol), methylamine (2.0 M solution in THF; 1 mL, 2 mmol) and THF (15 mL) afforded the compound as a yellow liquid. ^{1}H NMR (CDCl$_3$): δ = 13.18 (s, 1H), 8.98 (s, 1H), 8.10 (d, 1H), 8.03 (d, 1H), 7.67 (d, 1H), 3.41 (d, 3H); ^{13}C NMR (CDCl$_3$): δ = 168.2, 164.3, 143.4, 137.9, 134.7, 123.1, 120.8, 49.4; IR: ν = 3329 (ν$_{OH}$, br), 3067 (ν$_{CH}$, w), 2986 (ν$_{HC=N}$, w), 2840–2912 (ν$_{CH_3}$, br), 1618 (ν$_{C=N}$, s), 1570 (ν$_{NO_2}$, s), 1546 [ν$_{C=C(Ph)}$, w], 1524 [ν$_{C=C(Ph)}$, w], 1492 [ν$_{C=C(Ph)}$, w], 1465 [ν$_{C=C(Ph)}$, w], 1329 (ν$_{NO_2}$, s), 1133 cm^{-1} (ν$_{CO}$, br).

Schiff base 1c: Salicylaldehyde (0.24 g, 2 mmol), 4-bromo-2,6-dimethylaniline (0.4 g, 2 mmol) and ethanol (15 mL) afforded the compound as a yellow solid. ^{1}H NMR (CDCl$_3$): δ = 12.85 (s, 1H), 8.32 (s, 1H), 7.93 (t, 1H), 7.56 (t, 1H), 7.28 (d, 1H), 7.22 (s, 2H), 7.05 (d, 1H), 2.21 (s, 6H); ^{13}C NMR (CDCl$_3$): δ = 164.0, 160.9, 138.0, 132.4, 130.1, 129.8, 127.6, 127.1, 117.6, 117.3, 116.4, 18.2; IR: ν = 3342 (ν$_{OH}$, br), 3065 (ν$_{CH}$, w), 3031 (ν$_{CH}$, w), 2850–2925 (ν$_{CH_3}$, br), 1620 (ν$_{C=N}$, s), 1569 [ν$_{C=C(Ph)}$, w], 1523 [ν$_{C=C(Ph)}$, w], 1491 [ν$_{C=C(Ph)}$, w], 1467 [ν$_{C=C(Ph)}$, w], 1093 cm^{-1} (ν$_{CO}$, br).

Schiff base 1d: 5-Nitrosalicylaldehyde (0.33 g, 2 mmol), 4-bromo-2,6-dimethylaniline (0.4 g, 2 mmol) and ethanol (15 mL) afforded the compound as a yellow solid. ^{1}H NMR (CDCl$_3$): δ = 13.94 (s, 1H), 8.43 (s, 1H), 8.35 (d, 1H), 8.31 (d, 1H), 7.26 (s, 2H), 7.12 (d, 1H), 2.20 (s, 6H); ^{13}C NMR (CDCl$_3$): δ = 166.2, 165.3, 145.5, 139.9, 131.2, 130.2, 128.7, 128.5, 118.5, 118.0, 117.4, 18.1; IR: ν = 3337 (ν$_{OH}$, br), 3068 (ν$_{CH}$, w), 3036 (ν$_{CH}$, w), 2848–2922 (ν$_{CH_3}$, br), 1626 (ν$_{C=N}$, s), 1567(ν$_{NO_2}$, s), 1548 [ν$_{C=C(Ph)}$, w], 1527 [ν$_{C=C(Ph)}$, w], 1494 [ν$_{C=C(Ph)}$, w], 1467 [ν$_{C=C(Ph)}$, w], 1334 (ν$_{NO_2}$, s), 1096 cm^{-1} (ν$_{CO}$, br).

The spectroscopic properties of *Schiff bases* **1e** and **1f** have been reported.[11]

General Procedure for the Preparation of Schiff Base-Substituted Ruthenium Complexes 2a–f

The Schiff base-substituted ruthenium complexes **2a–f** were prepared and purified using well-established procedures.[11]

To a solution of the appropriate Schiff base (**1a–f**) in THF (10 mL), a solution of thallium ethoxide in THF (5 mL) was

added dropwise at room temperature. Immediately after the addition, a pale yellow solid formed and the reaction mixture was stirred for 2 hours at room temperature. Filtration of the solid under an argon atmosphere gave the respective thallium salt in quantitative yield. The salt was immediately used in the next step without further purification. A solution of the appropriate thallium salt in THF (5 mL) was added to a solution of the first generation Grubbs catalyst [RuCl$_2$(PCy$_3$)$_2$=CHPh] in THF (5 mL). The reaction mixture was stirred at room temperature for 4 hours. After evaporation of the solvent, the residue was dissolved in a minimal amount of benzene and cooled to 0 °C. The thallium chloride was removed by filtration. After evaporation of the solvent, the solid residue was recrystallised from pentane (– 70 °C) to give the respective Schiff base-substituted ruthenium complex (2a – f) in good yield as a brown solid.

Ruthenium Schiff base complex 2a: Ruthenium complex [RuCl$_2$(PCy$_3$)$_2$=CHPh] (1.20 g, 1.50 mmol), the thallium salt of ligand 1a (0.51 g, 1.50 mmol) and THF (20 mL) afforded the complex 2a as a brown solid; yield: 0.85 g (88%). ^{1}H NMR (CDCl$_3$): δ = 19.95 (d, 1H), 8.98 (d, 1H), 7.58 (t, 1H), 7.05 – 7.39 (br m, 7H), 6.86 (t, 1H), 3.57 (q, 3H), 3.27 (d, 3H), 1.28 – 1.86 (m, 30H); ^{31}P NMR (CDCl$_3$): δ = 52.44; IR: ν = 3063 (ν$_{CH}$, w), 3055 (ν$_{CH}$, w), 2840 – 2905 (ν$_{CH_3}$, br), 2810 (ν$_{CH_2}$, w), 1618 (ν$_{C=N}$, s), 1607 [ν$_{C=C(Ph)}$, w], 1584 [ν$_{C=C(Ph)}$, w], 1506 [ν$_{C=C(Ph)}$, w], 1458 (ν$_{CH_2}$, w), 1451 [ν$_{C=C(Ph)}$, w], 1107 (ν$_{Ru-O-Ph}$, w), 1005 (ν$_{skel.PCy_3}$, w), 568 (ν$_{Ru-O-Ph}$, w), 545 (ν$_{Ru-O-Ph}$, w), 512 (ν$_{Ru-Cl}$, w), 448 (ν$_{Ru-N}$, w), 442 cm^{-1} (ν$_{Ru-P}$ w); anal. calcd. (%) for RuC$_{33}$H$_{47}$ONClP (641.19): C 61.81, H 7.39, N 2.18; found: C 61.86, H 7.42, N 2.17.

Ruthenium Schiff base complex 2b: Ruthenium complex [RuCl$_2$(PCy$_3$)$_2$=CHPh] (1.20 g, 1.50 mmol), the thallium salt of ligand 1b (0.58 g, 1.50 mmol) and THF (20 mL) afforded the complex 2b as a brown solid; yield: 0.81 g (79%). ^{1}H NMR (CDCl$_3$): δ = 19.99 (d, 1H), 9.05 (d, 1H), 8.27 (d, 1H), 8.14 (d, 1H), 7.10 – 7.42 (m, 5H), 7.08 (d, 1H), 3.32 (d, 3H), 2.63 (q, 3H), 1.31 – 1.88 (m, 30H); ^{31}P NMR (CDCl$_3$): δ = 52.47; IR: ν = 3056 (ν$_{CH}$, w), 3050 (ν$_{CH}$, w), 2838 – 2900 (ν$_{CH_3}$, br), 2806 (ν$_{CH_2}$, w), 1616 (ν$_{C=N}$, s), 1603 [ν$_{C=C(Ph)}$, w], 1580 [ν$_{C=C(Ph)}$, w], 1552 (ν$_{NO_2}$, s), 1501 [ν$_{C=C(Ph)}$, w], 1451 (ν$_{CH_2}$, w), 1443 [ν$_{C=C(Ph)}$, w], 1335 (ν$_{NO_2}$, s), 1102 (ν$_{Ru-O-Ph}$, w), 1000 (ν$_{skel.PCy_3}$, w), 507 (ν$_{Ru-Cl}$, w), 443 (ν$_{Ru-N}$, w), 440 cm^{-1} (ν$_{Ru-P}$ w); anal. calcd. (%) for RuC$_{33}$H$_{46}$O$_3$N$_2$ClP (686.17): C 57.76, H 6.76, N 4.08; found: C 57.82, H 6.84, N 4.06.

Ruthenium Schiff base complex 2c: Ruthenium complex [RuCl$_2$(PCy$_3$)$_2$=CHPh] (1.20 g, 1.50 mmol), the thallium salt of ligand 1c (0.76 g, 1.50 mmol) and THF (20 mL) afforded the complex 2c as a brown solid; yield: 0.91 g (75%). ^{1}H NMR (CDCl$_3$): δ = 19.45 (d, 1H), 8.19 (d, 1H), 7.99 (d, 1H), 7.95 (d, 2H), 6.95 (d, 1H), 7.56 (t, 1H), 7.34 (t, 1H), 7.24 (t, 2H), 7.05 (t, 1H), 7.01 (s, 1H), 6.98 (s, 1H), 2.45 (q, 3H), 2.33 (s, 3H), 1.78 (d, 3H), 1.14 – 1.71 (m, 30H); ^{31}P NMR (CDCl$_3$): δ = 50.56; IR: ν = 3053 (ν$_{CH}$, w), 3038 (ν$_{CH}$, w), 2850 – 2961 (ν$_{CH_3, CH_2}$, br), 1603 (ν$_{C=N}$, s), 1582 [ν$_{C=C(Ph)}$, w], 1524 [ν$_{C=C(Ph)}$, w], 1469 [ν$_{C=C(Ph)}$, w], 1443 [ν$_{C=C(Ph)}$, w], 1065 (ν$_{Ru-O-Ph}$, w), 1004 (ν$_{skel.PCy_3}$, w), 801 (γ$_{CH}$, w), 787 (γ$_{Ph}$, w), 694 (ν$_{C-Br}$, s), 670 (ν$_{Ru-N}$, w), 558 (ν$_{Ru-O-Ph}$, w), 532 (ν$_{Ru-O-Ph}$, w), 498 (ν$_{Ru-Cl}$, w), 439 (ν$_{Ru-P}$ w); anal. calcd. (%) for RuC$_{40}$H$_{52}$ONClBrP (810.20): C 59.29, H 6.47, N 1.73; found: C 59.33, H 6.51, N 1.70.

Ruthenium Schiff base complex 2d: Ruthenium complex [RuCl$_2$(PCy$_3$)$_2$=CHPh] (1.20 g, 1.50 mmol), the thallium salt of ligand 1d (0.83 g, 1.50 mmol) and THF (20 mL) afforded the complex 2.d as a brown solid; yield: 0.93 g (72%). ^{1}H NMR (CDCl$_3$): δ = 19.49 (d, 1H), 8.24 (d, 1H), 8.06 (d, 1H), 8.05 (d,

1H), 7.97 (d, 2H), 7.54 (t, 1H), 7.26 (t, 2H), 7.14 (s, 1H), 7.09 (s, 1H), 7.03 (d, 1H), 2.49 (q, 3H), 2.40 (s, 3H), 1.84 (d, 3H), 1.15 – 1.83 (m, 30 H); ^{31}P NMR (CDCl$_3$): δ = 50.66; IR: ν = 3048 (ν$_{CH}$, w), 3035 (ν$_{CH}$, w), 2846 – 2957 (ν$_{CH_3, CH_2}$, br), 1598 (ν$_{C=N}$, s), 1577 [ν$_{C=C(Ph)}$, w], 1544 (ν$_{NO_2}$, s), 1521 [ν$_{C=C(Ph)}$, w], 1462 [ν$_{C=C(Ph)}$, w], 1441 [ν$_{C=C(Ph)}$, w], 1326 (ν$_{NO_2}$, s), 1048 (ν$_{Ru-O-Ph}$, w), 1001 (ν$_{skel.PCy_3}$, w), 797 (γ$_{CH}$, w), 783 (γ$_{Ph}$, w), 690 (ν$_{C-Br}$, s), 664 (ν$_{Ru-N}$, w), 546 (ν$_{Ru-O-Ph}$, w), 518 (ν$_{Ru-Cl}$, w), 432 cm^{-1} (ν$_{Ru-P}$ w); anal. calcd. (%) for RuC$_{40}$H$_{51}$O$_3$N$_2$ClBrP (855.18): C 56.18, H 6.01, N 3.28; found: C 56.27, H 6.07, N 3.25.

The spectroscopic properties of *ruthenium Schiff base complexes* 2e and 2f have been reported.[11]

General Procedure for the Preparation of Schiff Base-Substituted Bimetallic Ruthenium Complexes 3a – f

To a solution of the Schiff base-substituted ruthenium complex (2a – f) in benzene (25 mL) was added a solution of Ru-dimer [RuCl$_2$(p-cymene)]$_2$ in benzene (25 mL). The solution was stirred for 4 h at room temperature during which time a solid precipitate formed from the solution. The solid was isolated by filtration under inert atmosphere and washed with benzene (3 × 30 mL) to remove the [(p-cymene)RuCl$_2$PCy$_3$] byproduct and any unreacted starting materials. After recrystallisation from chlorobenzene/pentane and additional washing with 2 × 10 mL of pentane to remove the residual chlorobenzene, the product was dried under vacuum, affording the bimetallic Schiff base substituted ruthenium complexes 3a – f in good yields.

Bimetallic Schiff base-substituted ruthenium complex 3.a: Ruthenium complex 2a (0.64 g, 1 mmol) and the dimer [RuCl$_2$(p-cymene)]$_2$ (0.61 g, 1 mmol) afforded the complex 3a as an orange-green powder; yield: 0.419 g (63%). ^{1}H NMR (CDCl$_3$): δ = 19.97 (d, 1H), 9.03 (d, 1H), 7.64 (t, 1H), 7.09 – 7.44 (br m, 7H), 7.01 (t, 1H), 5.58 (d, 1H), 5.46 (d, 1H), 5.29 (d, 1H), 5.15 (d, 1H), 3.31 (d, 3H), 2.92 (septet, 1H), 2.19 (s, 3H), 1.35 (d, 3H), 1.32 (d, 3H); IR: ν = 3060 (ν$_{CH}$, w), 3054 (ν$_{CH}$, w), 2838 – 2901 (ν$_{CH_3}$, br), 2806 (ν$_{CH_2}$, w), 1617 (ν$_{C=N}$, s), 1605 [ν$_{C=C(Ph)}$, w], 1583 [ν$_{C=C(Ph)}$, w], 1506 [ν$_{C=C(Ph)}$, w], 1455 [ν$_{C=C(Ph)}$, w], 1449 (ν$_{CH_2}$, w), 1382 (skel.$_{i-Pr}$, m), 1361 (skel.$_{i-Pr}$, m), 1106 (ν$_{Ru-O-Ph}$, w), 1003 (ν$_{skel.PCy_3}$, w), 773 (γ$_{CH}$, w), 564 (ν$_{Ru-O-Ph}$, w), 544 (ν$_{Ru-O-Ph}$, w), 512 (ν$_{Ru-Cl}$, w), 440 cm^{-1} (ν$_{Ru-N}$, w); anal. calcd. (%) for Ru$_2$C$_{25}$H$_{28}$ONCl$_3$ (666.96): C 45.02, H 4.23, N 2.10; found: C 45.10, H 4.25, N 2.11.

Bimetallic Schiff base-substituted ruthenium complex 3b: Ruthenium complex 2b (0.69 g, 1 mmol) and the dimer [RuCl$_2$(p-cymene)]$_2$ (0.61 g, 1 mmol) afforded the complex 3b as an orange-green powder; yield: 0.476 g (67%). ^{1}H NMR (CDCl$_3$): δ = 20.02 (d, 1H), 9.08 (d, 1H), 8.34 (d, 1H), 8.19 (d, 1H), 7.53 (d, 2H), 7.45 (t, 1H), 7.38 (t, 2H), 7.16 (d, 1H), 5.64 (d, 1H), 5.52 (d, 1H), 5.33 (d, 1H), 5.19 (d, 1H), 3.36 (d, 3H), 2.96 (septet, 1H), 2.21 (s, 3H), 1.40 (d, 3H), 1.37 (d, 3H); IR: ν = 3054 (ν$_{CH}$, w), 3047 (ν$_{CH}$, w), 2835 – 2898 (ν$_{CH_3}$, br), 2802 (ν$_{CH_2}$, w), 1615 (ν$_{C=N}$, s), 1600 [ν$_{C=C(Ph)}$, w], 1577 [ν$_{C=C(Ph)}$, w], 1550 (ν$_{NO_2}$, s), 1500 [ν$_{C=C(Ph)}$, w], 1447 [ν$_{C=C(Ph)}$, w], 1441 (ν$_{CH_2}$, w), 1382 (skel.$_{i-Pr}$, m), 1363 (skel.$_{i-Pr}$, m), 1332 (ν$_{NO_2}$, s), 1098 (ν$_{Ru-O-Ph}$, w), 997 (ν$_{skel.PCy_3}$, w), 768 (γ$_{CH}$, w), 558 (ν$_{Ru-O-Ph}$, w), 540 (ν$_{Ru-O-Ph}$, w), 503 (ν$_{Ru-Cl}$, w), 437 cm^{-1}) (ν$_{Ru-N}$, w); anal. calcd. (%) for Ru$_2$C$_{25}$H$_{27}$O$_3$N$_2$Cl$_3$ (711.94): C 42.17, H 3.82, N 3.93; found: C 42.24, H 3.84, N 3.91.

Bimetallic Schiff base-substituted ruthenium complex 3c: Ruthenium complex 2c (0.81 g, 1 mmol) and the dimer [RuCl$_2$(p-cymene)]$_2$ (0.61 g, 1 mmol) afforded the complex

3c as an orange powder; yield: 0.511 g (61%). ^{1}H NMR (CDCl$_3$): δ = 19.48 (d, 1H), 8.21 (d, 1H), 8.12 (d, 1H), 8.06 (d, 2H), 7.72 (t, 1H), 7.44 (t, 2H), 7.38 (t, 1H), 7.12 (t, 1H), 7.09 (s, 1H), 7.06 (d, 1H), 7.02 (s, 1H), 5.45 (d, 1H), 5.30 (d, 1H), 5.17 (d, 1H), 5.06 (d, 1H), 2.84 (septet, 1H), 2.06 (s, 3H), 2.03 (s, 3H), 1.89 (d, 3H), 1.28 (d, 3H), 1.24 (d, 3H); IR: ν = 3052 (ν_{CH}, w), 3038 (ν_{CH}, w), 2848–2968 (ν_{CH_3}, br), 1601 ($\nu_{C=N}$, s), 1579 [$\nu_{C=C(Ph)}$, w], 1523 [$\nu_{C=C(Ph)}$, w], 1466 [$\nu_{C=C(Ph)}$, w], 1443 [$\nu_{C=C(Ph)}$, w], 1385 (skel.$_{i\text{-}Pr}$, m), 1367 (skel.$_{i\text{-}Pr}$, m), 1062 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 1003 ($\nu_{skel.PCy_3}$, w), 801 ($\gamma_{CH}$, w), 784 ($\gamma_{CH}$, w), 692 ($\nu_{C\text{-}Br}$, s), 666 ($\nu_{Ru\text{-}N}$, w), 554 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 527 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 492 cm^{-1} ($\nu_{Ru\text{-}Cl}$, w); anal. calcd. (%) for Ru$_2$C$_{32}$H$_{33}$ONCl$_3$Br (835.97): C 45.97, H 3.98, N 1.68; found: C 46.03, H 4.01, N 1.65.

Bimetallic Schiff base-substituted ruthenium complex 3d: Ruthenium complex **2d** (0.86 g, 1 mmol) and the dimer [RuCl$_2$(p-cymene)]$_2$ (0.61 g, 1 mmol) afforded the complex **3d** as a dark orange powder; yield: 0.602 g (68%). ^{1}H NMR (CDCl$_3$): δ = 19.50 (d, 1H), 8.36 (d, 1H), 8.31 (d, 1H), 8.10 (d, 2H), 7.76 (t, 1H), 7.71 (d, 1H), 7.43 (t, 2H), 7.15 (d, 1H), 7.11 (s, 1H), 7.07 (s, 1H), 5.49 (d, 1H), 5.36 (d, 1H), 5.21 (d, 1H), 5.11 (d, 1H), 2.86 (septet, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 1.96 (d, 3H), 1.31 (d, 3H), 1.29 (d, 3H); IR: ν = 3045 (ν_{CH}, w), 3031 (ν_{CH}, w), 2844–2963 (ν_{CH_3}, br), 1597 ($\nu_{C=N}$, s), 1576 [$\nu_{C=C(Ph)}$, w], 1541 (ν_{NO_2}, s), 1517 [$\nu_{C=C(Ph)}$, w], 1458 [$\nu_{C=C(Ph)}$, w], 1440 [$\nu_{C=C(Ph)}$, w], 1389 (skel.$_{i\text{-}Pr}$, m), 1369 (skel.$_{i\text{-}Pr}$, m), 1322 (ν_{NO_2}, s), 1044 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 995 ($\nu_{skel.PCy_3}$, w), 793 ($\gamma_{CH}$, w), 779 ($\gamma_{CH}$, w), 683 ($\nu_{C\text{-}Br}$, s), 659 ($\nu_{Ru\text{-}N}$, w), 541 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 514 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 482 cm^{-1} ($\nu_{Ru\text{-}Cl}$, w); anal. calcd. (%) for Ru$_2$C$_{32}$H$_{32}$O$_3$N$_2$Cl$_3$Br (880.95): C 43.63, H 3.66, N 3.18; found: C 43.71, H 3.70, N 3.17.

Bimetallic Schiff base-substituted ruthenium complex 3e: Ruthenium complex **2e** (0.79 g, 1 mmol) and the dimer [RuCl$_2$(p-cymene)]$_2$ (0.61 g, 1 mmol) afforded the complex **3e** as a yellow-green powder; yield: 0.597 g (73%). ^{1}H NMR (CDCl$_3$): δ = 19.71 (d, 1H), 8.12 (d, 1H), 7.96 (d, 2H), 7.55 (t, 1H), 7.11-7.44 (br m, 8 H), 6.66 (t, 1H), 5.42 (d, 1H), 5.27 (d, 1H), 5.12 (d, 1H), 5.01 (d, 1H), 3.41 (septet, 1H), 2.81 (septet, 1H), 2.25 (septet, 1H), 2.01 (s, 3H), 1.67 (d, 3H), 1.29 (d, 3H), 1.26 (d, 3H), 1.21 (d, 3H), 0.82 (dd, 6H); IR: ν = 3059 (ν_{CH}, w), 3040 (ν_{CH}, w), 2857–2961 (ν_{CH_3}, br), 1607 ($\nu_{C=N}$, s), 1586 [$\nu_{C=C(Ph)}$, w], 1527 [$\nu_{C=C(Ph)}$, w], 1469 [$\nu_{C=C(Ph)}$, w], 1445 [$\nu_{C=C(Ph)}$, w], 1383 (skel.$_{i\text{-}Pr}$, m), 1364 (skel.$_{i\text{-}Pr}$, m), 1070 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 1009 ($\nu_{skel.PCy_3}$, w), 806 ($\gamma_{CH}$, w), 794 ($\gamma_{CH}$, w), 688 ($\nu_{Ru\text{-}N}$, w), 564 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 537 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 508 cm^{-1} ($\nu_{Ru\text{-}Cl}$, w); anal. calcd. (%) for Ru$_2$C$_{36}$H$_{42}$ONCl$_3$ (813.18): C 53.17, H 5.21, N 1.72; found: C 53.23, H 5.24, N 1.74.

Bimetallic Schiff base-substituted ruthenium complex 3f: Ruthenium complex **2f** (0.83 g, 1 mmol) and the dimer [RuCl$_2$(p-cymene)]$_2$ (0.61 g, 1 mmol) afforded the complex **3f** as an orange powder; yield: 0.587 g (68%). ^{1}H NMR (CDCl$_3$): δ = 19.81 (d, 1H), 8.32 (d, 1H), 8.22 (d, 1H), 8.16 (d, 1H), 7.34 – 7.98 (br m, 8H), 7.06 (d, 1H), 5.39 (d, 1H), 5.25 (d, 1H), 5.08 (d, 1H), 4.97 (d, 1H), 3.51 (septet, 1H), 2.77 (septet, 1H), 2.32 (septet, 1H), 1.98 (s, 3H), 1.74 (d, 3H), 1.34 (d, 3H), 1.20 (d, 3H), 1.16 (d, 3H), 0.88 (dd, 6H); IR: ν = 3054 (ν_{CH}, w), 3037 (ν_{CH}, w), 2850–2965 (ν_{CH_3}, br), 1602 ($\nu_{C=N}$, s), 1582 [$\nu_{C=C(Ph)}$, w], 1550 (ν_{NO_2}, s), 1528 [$\nu_{C=C(Ph)}$, w], 1464 [$\nu_{C=C(Ph)}$, w], 1444 [$\nu_{C=C(Ph)}$, w], 1387 (skel.$_{i\text{-}Pr}$, m), 1366 (skel.$_{i\text{-}Pr}$, m), 1331 (ν_{NO_2}, s), 1100 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 1057 ($\nu_{skel.PCy_3}$, w), 798 ($\gamma_{CH}$, w), 785 ($\gamma_{CH}$, w), 678 ($\nu_{Ru\text{-}N}$, w), 557 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 529 ($\nu_{Ru\text{-}O\text{-}Ph}$, w), 496 cm^{-1} ($\nu_{Ru\text{-}Cl}$, w); anal. calcd. (%) for Ru$_2$C$_{36}$H$_{41}$O$_3$N$_2$Cl$_3$ (858.16): C 50.38, H 4.82, N 3.26; found: C 50.44, H 4.85, N 3.25.

General Procedure for Ring-Opening Metathesis Polymerisations (ROMP)

In a typical ROMP experiment 0.005 mmol of the catalyst as a solution in chlorobenzene (0.1004 M) was transferred into a 15-mL vessel followed by the addition the appropriate amount of monomer solution (200 equivalents for cyclooctene and 800 equivalents for the norbornene derivatives) in chlorobenzene. The reaction mixture was then kept stirring at 70 °C for 4 hours. To stop the polymerisation reaction, 2–3 mL of an ethyl vinyl ether/BHT solution was added and the solution was stirred for 0.5 hour to make sure that the deactivation of the active species was completed. The solution was poured into methanol (50 mL containing 0.1% BHT) and the polymers were precipitated and dried under vacuum overnight.

General Procedure for Ring-Closing Metathesis Reactions (RCM)

All reactions were performed on the benchtop in air by weighing 5 mol % of the catalyst into a dry NMR tube and dissolving the solid in 1 mL of C$_6$D$_5$Cl. A solution of the appropriate substrate (0.1 mmol) in C$_6$D$_5$Cl (1 mL) was added. The tube was then capped, wrapped with parafilm, and shaken for 4 hours at 55 °C for catalytic systems **2** and at 70 °C for catalytic systems **3**. Product formation (all reaction products were unambiguously identified previously[12b]) and diene disappearance were monitored by integrating the allylic methylene peaks.

Acknowledgements

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